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MATERIALS AND PREPARATION THEREOF

EXHIBIT 1

[This electronic file contains the English translation of three incomplete Chinese articles.]

[Article No. 1]

[Only the end of the article is available in the original Chinese copy.]

Conclusion

The microscopic appraisal and naming of sedimentary rocks is one of the important basics for phase analysis, paleo-geographical study and petro-lithostratigraphical research. Sedimentary rocks were seldom subjected to microscopic appraisals. As a result, they were often given incorrect nomenclatures. A great deal of research work is still needed in this area. It is advisable to devote separate chapters to sedimentary rocks in geological reports. This is the purpose of this article and the wish of the author. The author welcomes any suggestions for improvements on this article as well as any comments on possible errors in this article.

Reference Material

Mantle Rocks and Native Gold

Reports about the discovery of native gold in mantle rocks have appeared several times in recent years. For example:

1. Native gold was found in super magnesioferrite rocks in the mantle layer in Tibet, China. It was found along with major constituent minerals such as olivine, pyroxene, picotite, and minor constituent minerals such as almandine, moissanite, zircon, corundum, and chromium carbide.
2. Native gold was found in the mantle layer at the lower part of the Oysh Fault in the Indian Ocean. It was in the form of 20 gold grains, approximately 0.05 mm in size, assuming an allotype crystal shape (lamellar, dendritic, or amoeboid), and co-existing with sulfides. The native gold grains were directly surrounded by serpentine orthopyroxene olivine. The fissures were visibly filled with carbonates. Studies on the orthopyroxene olivine revealed that the mineralization of gold in the fault was related to the carbonation process.
3. Native gold was found in the alkaline *[original text illegible]* rocks of the Mesozoic era in the Kaliri-Kela region of the Soviet Union. The gold, embedded in *[original text illegible]* minerals and 0.2-1mm in size, co-existed with quartz and sulfides. It contained Au 94.7--95.7% and Ag 4.2--5.2%. Studies revealed that the native gold was associated with the bowenite transforming process.

Judging from the distribution of native gold in the mantle rocks and the crust rocks, foreign researchers contended that the substitution between the earth's inner part (the

mantle) and the earth's crust provides a major preparation stage for the petrometallogeny of endogenic gold deposits. The high-temperature substitution of the earth's matter causes the unevenness in the distribution of metals in the differentiation products deep down in the earth. In the reduction conditions of the mantle layer, gold remains in a not-so-active (relatively stable) state. It resides in magnesioferrite and super magnesioferrite rocks that contain sulfides. The substitution process in the inner part (the mantle) of the earth may generate minerals with an original content of 50% gold. In the oxidation environment of the crust, the gold gets re-distributed and resides in rocks of the gabbro and granite families.

Sources of the information presented above:

1. 中国地质科学院地质研究所所刊, 1986, 第14号, 91—106.
2. «Изв.АН СССР», Сер.геол., 1987, №12, 124—128.
3. «Докл.АН СССР», 1988, 299, №3, 715—716,
4. «Докл.АН СССР», 1988, 299, №5, 1233—1237.

[Translation of Item 1:]

1. Journal of the Geological Research Institute, Chinese Academy of Geological Sciences, 1986,
Vol. 14, pp. 91-106.

This article was submitted by Yi Shi.

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[Article No. 2]

[The first page of this article is missing in the original Chinese copy. The translator has moved the "Abstract" part from the end of the article to the beginning to substitute for the missing first page.]

Triphylite-Lithiophilite Series in China

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Key Words: triphylite, lithiophilite, isomorphism, cell dimensions, IR spectra

Abstract

Triphylite-lithiophilite, a perfect isomorphous series, has been found in six mineral occurrences in China. Of these, four are in the rare-metal granite pegmatites of the Xinjiang Autonomous Region, where all of the samples are lithiophilite. The Mn-rich features are also observed in other Fe and Mn minerals of Xinjiang pegmatites. In 1984, a few specimens of triphylite were discovered in the rare-metal pegmatite in Nanping County, Fujian Province. The mineral is one of the few Fe and Mg-richest triphylites in the world. Another triphylite discovery occurs in the pegmatite in Shangxian County, Shanxi Province. By now, all constituents of a complete triphylite-lithiophilite series have been found in China, whose mineralogical properties are all listed in this article.

Researches on the chemical composition of triphylite-lithiophilite show that, besides the major constituents Fe^{2+} and Mn^{2+} , the cations at the octahedral M(2) site in the minerals are Mg^{2+} , Ca^{2+} , Fe^{3+} . The highest MgO content is 7.38 wt%. Generally speaking, Mg^{2+} replaces Fe^{2+} easily, while Ca^{2+} sometimes substitutes for Mn^{2+} at the R(2) site. Pure triphylite has not yet been found in nature and $\text{LiFe}[\text{PO}_4]$ contents of all native triphylites are lower than 80%. Nevertheless, there are very pure lithiophilites in nature.

The article illustrates the relationships of the chemical composition (Fe/Mn) to physical properties, optical properties and unit cell dimensions of the series. With the increase in the Fe/Mn ratio, the specific gravity and the index of refraction will increase, the cell parameters will decrease, and the optical axial angle will vary regularly. The rising of the Mg^{2+} and Ca^{2+} contents of the minerals, on the other hand, will also cause an obvious variation in the above-mentioned properties.

An IR spectral analysis of the four triphylite-lithiophilite samples collected in China is conducted to determine the correlation between the chemical composition and the IR absorption peaks. The results show that there exists a good linear correlation between the absorption peaks from the $475\text{-}456\text{cm}^{-1}$ range on the one hand and the

chemical composition on the other. It is, therefore, feasible to use the IR spectra for the semi-quantitative determination of the chemical composition of this series.

[Incomplete sentence] all constituents of this series have been found in China. Undoubtedly, it is now necessary to conduct a systematic, comparative study of China's triphylite-lithiophilite series. This article will present its discussion on this subject with an emphasis on the Nanping triphylite deposit as the authors have done a lot of research in that respect.

I. Occurrences and Paragenetic Association

The six triphylite-lithiophilite occurrences discovered in China so far all exist in relatively well-evolved rare-metal granite pegmatites, which bear industrial significance. In the pegmatites, this series basically is found in the center or the core of the textural seams. It is in big lumps, mostly semi-euhedral or allo-hedral. It is so rich in the pegmatites that it is one of the constituents of the pegmatite formation. The series co-exists with quartz, cleavelandite, granular albite, microcline, lamina muscovite, beryl, columbite-tantalite, and common lithium minerals (spodumene, amblygonite, etc.). Depending on locations, each occurrence has some unique features. For example, the lithiophilite (Fe minerals) at Qinghe, Xinjiang is deposited in granite pegmatite of relatively advanced beryl mineralization, with a lot of beryl around but no spodumene or amblygonite. The triphylite (Mn minerals) at Shangxian County, Shanxi and Kelumute, Xinjiang has no paragenetic amblygonite. In terms of formation, the series was generally formed in the later stage of the primary crystallization process of the pegmatites. This theory is corroborated by the position of the series in the pegmatite seams. In terms of mineralization, the occurrence of the series often reflects the rare-metal mineralization level of the pegmatites. Generally speaking, the higher the content, the higher the mineralization level.

The occurrence of the Nanping triphylite is somewhat different from occurrences of the same category both at home and abroad. It is deposited in Pegmatite Vein No. 31, which is the largest pegmatite vein at Nanping County, Fujian Province and has the highest level of Ta (Nb), Li, Be, Sn mineralization and the most developed textural seams. The triphylite is visible in the quartz-amblygonite textural seam. It runs, in thin veins of generally 10-20 cm long and 0.1-0.5 cm wide, through lumps of amblygonite of an early formation. The vein walls are usually studded with damourite. The veins are full of triphylite, with a small quantity of paragenetic childrenite, amblygonite of a later formation, quartz and iron pyrite. The formation of the Nanping triphylite occurred after the differentiation of the primary crystallization process was over and the pegmatites were substantially consolidated. At a later time, trickles of rare-metal rich fluids filled and crystallized in the fissures of the amblygonite lumps. The triphylite content is low in the pegmatites. Moreover, it has been found only in one region so far.

Due to the later-stage fluid activity and superficial oxidation, all triphylite-lithiophilite minerals demonstrate signs of instability under the substitution corrosion and superficial oxidation effects. In the test slices, the sectional surface and its edges often show non-transparent or half-transparent brown spots of corroded minerals, which are mainly sicklerite: $\text{Li}_{1-x}(\text{Mn}_{1-x}, \text{Fe}^{3+}_x)[\text{PO}_4]$. It may be assumed that those corroded minerals are the product of the Li leaching and the oxidation of Fe^{2+} to Fe^{3+} . Among the six occurrences in China, the lithiophilite at Keketuohai, Xinjiang has seen the most serious corrosion. On the ground surface, the corrosion has transformed most of the lithiophilite to sicklerite and, to a lesser extent, dickinsonite^[5]. The Nanping triphylite is less corroded. Test slices show only a limited amount of green or brown corroded minerals (sicklerite) and sericite on the edges and in the fissures. Relatively speaking, the Qinghe lithiophilite (Fe minerals) in Xinjiang is the least corroded. It still looks fresh on the ground surface.

II. Chemical Composition

The authors have conducted comprehensive chemical analyses of the Nanping triphylite and the Qinghe lithiophilite. The authors have also conducted comparative studies of the comprehensive chemical analysis data for 47 samples collected all over the world since 1920 (including samples from the other four Chinese occurrences). Table 1 lists the analysis results of 26 more representative samples out of the 47. As is shown in Table 1, the Li content varies substantially, but generally only a very small amount of Na^+ replaces Li^+ at the octahedral M(1) site. Some samples have a relative high content of Fe^{3+} . For example, the Nanping triphylite has a 5.91% content of Fe_2O_3 while the Shangxian triphylite has 9.62%. A careful analysis of the data in the table will also reveal that the Li^+ content and the Fe^{3+} content have a negative correlation while the Fe^{3+} content and the H_2O^+ content have a positive correlation. Such correlations are even more obvious among the domestic samples. This phenomenon may be due to the fact that the test samples contain sicklerite molecules $\text{Li}_{1-x}(\text{Mn}_{1-x}, \text{Fe}^{3+}_x)[\text{PO}_4]$. The vacancy taken by those molecules has made it possible for H_2O to enter the mineral crystal lattice. It is generally believed that those molecules assume the form of independent sicklerite minerals and get mixed with the triphylite-lithiophilite sample because sicklerite is the most common and the first oxidation product of the series. The partial substitution of Fe^{2+} by Fe^{3+} also causes some loss of Li^+ in the series. The difference between triphylite and sicklerite (the corrosion product) in physical properties such as color and transparency is due to this loss, too.

Table 1 Chemical composition, refraction indices, optic angles and specific gravities of talphite-lithophilite series

[illegible]

注: 重量百分数: SiO_2 0.40, Al_2O_3 0.84, TiO_2 0.11, K_2O 0.06, F^- 0.31, Sr 607 ppm.

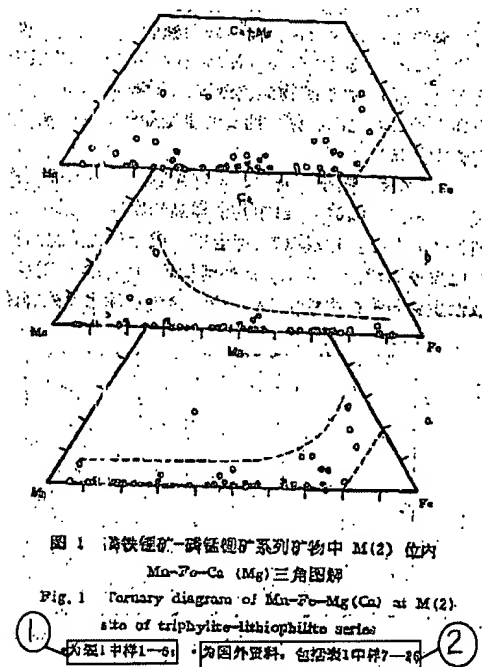
SiO₂ 0.40, Al₂O₃ 0.12, TiO₂ 0.09, K₂O 0.01, F⁻ 0.29.

样)、测试单位:北京轴矿地质研究所。

- [Key:] (1) [place names]
- | | |
|----------------------|------------------------|
| 1 Nanping, Fujian | 2 Shangxian, Shanxi |
| 3 Qinghe, Xinjiang | 4 Xiaohusite, Xinjiang |
| 5 Kelutemu, Xinjiang | 6 Keketuohai, Xinjiang |
| 7 U.S.A. | 8 West Germany |
| 9 West Germany | 10 Soviet Union |
| 11 Finland | 12 U.S.A. |
| 13 Sweden | 14 Sweden |
| 15 Canada | 16 Argentina |
| 17 Rwanda | 18 Soviet Union |
| 19 U.S.A. | 20 U.S.A. |
| 21 Soviet Union | 22 Australia |
| 23 U.S.A. | 24 Sweden |
| 25 U.S.A. | 26 U.S.A. |
- (2) Item No.
 (3) Place of Origin
 (4) Source of Information
 (5) Year of Publication
 (6) Authors of This Article
 (7) Shanxi Geology and Minerals Bureau
 (8) Authors of This Article
 (9) Zhou Tianren
 (10) Other
 (11) Total
 (12) Notes: The "Other" in Sample No. 1 refers to...
 (13) The "Other" in Sample No. 3 refers to...
 (14) Tests on Samples No. 1 and 3 were conducted by Beijing Uranium Minerals and Geology Research Institute.

The entry of cations at the octahedral M(2) site of the triphylite-lithiophilite series is the most important indication of the chemical composition changes in the series. The Mn-Fe-Mg, Mn-Fe-Ca and Mn-Fe-Mg+Ca ternary diagram below (Fig. 1) shows the positions of the 47 chemical analysis samples collected. The small circles in the diagram refer to the 6 domestic occurrences. It is easy to see that Mg and Ca generally replace, by a specific amount or in a finite isomorphous form, Fe and Mn in the minerals (the range below the dotted line in Fig. 1) and that the maximum atomic weight of Mg+Ca at the M(2) site does not exceed 27%. No LiCa[PO₄] or LiMg[PO₄] minerals have been found in nature so far. Maybe no suitable conditions for the formation of such minerals exist in pegmatites. Although both of them may enter the M(2) site, Mg²⁺ and Ca²⁺ demonstrate different characteristics. As is shown in Fig. 1-a, the Mg isomorphous replacement range increases as it moves closer to the Fe end member. The maximum concentration of Mg at the M(2) site may be as high as 26.7%^[4]. On the other hand, the case with Ca is entirely different. Ca is relatively concentrated towards the Mn end member (Fig. 1-b). This means

that Mg^{2+} is more likely to replace Fe^{2+} in an isomorphous form while Ca^{2+} is more likely to replace Mn^{2+} . It is due to the similarity of chemical properties between the Mg^{2+} and Fe^{2+} crystals and between the Ca^{2+} and Mn^{2+} crystals. However, there is one exception in Fig. 1-a (Sample No. 16 in Table 1). The mineral is positioned above the dotted line. According to Hurlbut (1968)^[18], that particular mineral was not formed through the normal crystallization process. Instead, a solid solution was formed, through crystallization, from the initial melted pegmatite solution. After the temperature dropped, the solid solution, which was composed of $(\text{Mn}, \text{Fe}, \text{Ca}, \text{Mg})_3[\text{PO}_4]_2(82\%)+\text{Li}(\text{Mn}, \text{Fe}, \text{Ca})[\text{PO}_4](18\%)$, disintegrated into dual-phase compound strips of triphylite and lithiophilite. During the process, conditions might become favorable for Mg^{2+} to enter the lithiophilite, hence the unusually high Mg content in that particular sample. Triphylite-lithiophilite minerals formed through normal crystallization in nature generally have their chemical composition indicators positioned below the dotted line -- mostly near the bottom line -- in Fig. 1.



[Key:] (1) Samples No. 1-6 in Table 1.
(2) Data on foreign samples, including Samples No. 7-26 in Table 1.

It should be noted that there are no dots in the small triangle at the lower right-hand corner of Fig. 1-a or 1-c. It means that up till now no near-end-member triphylite of the $\text{LiFe}[\text{PO}_4]$ molecular content greater than 80% has been found. The reason is simple: the closer to the Fe end member, the greater the Mg replacement. However, it is possible to have man-made pure triphylite by synthetic means^[2]. As for the other end member, high-purity lithiophilite does exist in nature. Its $\text{LiMn}[\text{PO}_4]$ molecular content may be over 98%.

Interestingly, the six domestic samples are more or less equally spaced from the Mn end member to the Fe end member in Fig. 1. This means that the constituents of the triphylite-lithiophilite series in China have all been found. The four samples near the Mn end member all come from the Altai region and its vicinity in Xinjiang. It seems that most pegmatites in Xinjiang are Mn-rich and the associated minerals also demonstrate this characteristic. The domestic Fe-rich end member is found in the Nanping pegmatites in Fujian Province: up to 0.889 of Fe/(Fe+Mn). This value and the Mg content value are only lower than those of the triphylite that Chapman (1948) found in the pegmatites in New Hampshire, U.S.A.^[4], but similar to those of the triphylite found in the rare-metal granite pegmatites in Morocco^[3]. The residual fluid phase of the original crystallization in the Nanping pegmatites is relatively poor in Mn and rich in Fe and Mg. For example, the Fe/Mn ratio in its paragenetic childrenite is 1.78^[20]. There are also associated lazulite^[21] and fibrous dravite^[22], which were formed as a result of replacement corrosion at approximately the same time as with the triphylite. Fig. 1 also shows that the Mg content in the six domestic samples is relatively higher than foreign samples, but the Ca content is lower.

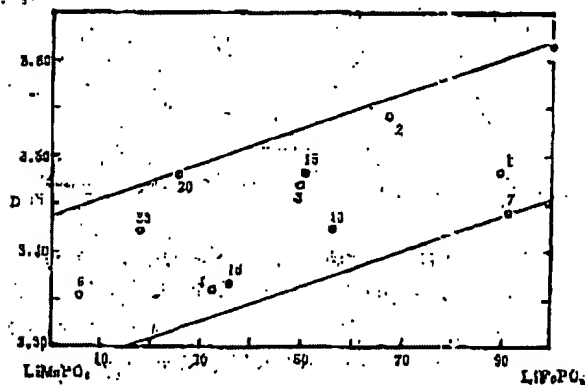
The conclusion drawn from the above discussion is that the Mg and Ca content in native triphylite-lithiophilite depends not only on the concentration of the two elements in the fluid phase of their formation, but also on the Fe(Mn) content of the series. In other words, Fe end member minerals are generally Mg-rich while Ca is more likely to go into the Mn-rich lithiophilite.

III. Physical and Optical Properties

1. Colors: The colors of the triphylite-lithiophilite series minerals vary systematically with the changes in the chemical composition. The Nanping triphylite has a grayish green color. The Shangxian triphylite is yellowish green and the Qinghe lithiophilite is grayish brown with a green touch. Samples No. 4, 5 and 6 (Table 1) which are closer to the Mn end member are light yellowish pink, yellowish brown, and light brown with a yellow touch respectively. The minerals near the Fe end member have dark colors with a green touch while the minerals near the Mn end member have lighter colors with a yellow touch. The minerals in the center section between the two end members have medium-depth colors. Foreign documents have drawn the same conclusion. This means that the colors of minerals may be used, to a certain extent, to determine the composition of the minerals.

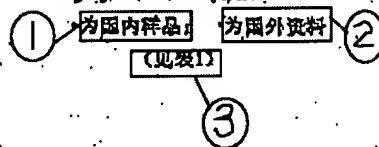
2. Specific Gravity: The specific gravity of the Nanping, Qinghe and Keketuohai samples is measured in their respective Coleridge solutions with a pycnometer with an accuracy error rate of 0.02. The specific gravity of the other samples in Table 1 generally has an accuracy error rate of ± 0.01 –0.02. Fig. 2 displays the data on five domestic samples and six foreign samples. It is obvious that the composition of the samples has a linear correlation with their specific gravity. The specific gravity increases with the increase of the $\text{LiFe}[\text{PO}_4]$ molecules. Man-made pure $\text{LiFe}[\text{PO}_4]$

has the greatest specific gravity: 3.615g/cm^3 ^[23]. The scattering of the indicator dots in Fig. 2 is caused by several factors, such as the Mg, Ca and Fe^{3+} content in the minerals and the measuring errors. For example, the specific gravity of the three samples (Nos. 1, 7 and 16) that contain more than 5% MgO is relatively small. In particular, Sample No. 7, which has the highest Mg content, has a noticeably low specific gravity. An increase in the Fe^{3+} and Ca content may also cause the specific gravity to decrease. Those factors have made the relationship between the Fe/Mn content in the minerals and their specific gravity more complicated.



图·2 磷铁锂矿-磷锰锂矿系列中化学成分与比重间的关系

Fig. 2 Specific gravities plotted against chemical composition of triphylite-lithiophilite series

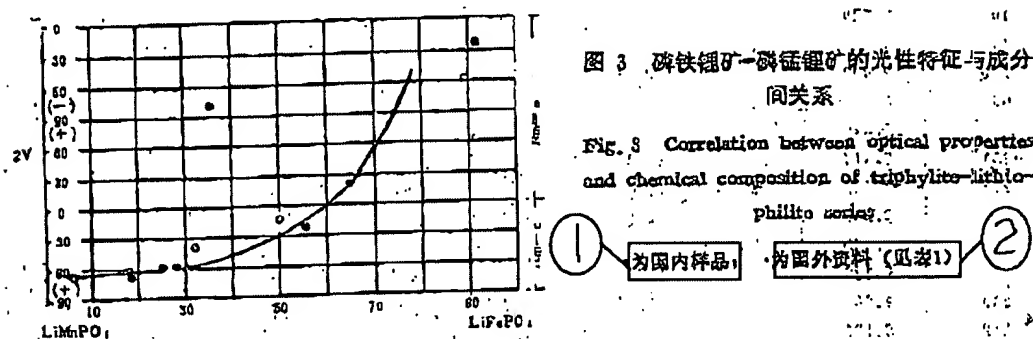


[Key:] (1) Domestic samples
(2) Data on foreign samples
(3) (See Table 1)

3. Optical Properties: Table 1 lists the authors' measurements of the optical axial angles, the refraction indices and the optical directions of the Nanping triphylite and the Qinghe lithiophilite. The optical axial angle is measured on a five-axis rotating table with an accuracy error rate of $\pm 2^\circ$. The optical axial angle of the Qinghe lithiophilite is so small that the accuracy is adversely affected (error rate $\pm 4^\circ$). The refraction index is measured by an oil immersion method under a sodium lamp, with an accuracy rate of 0.001. The optical bearing test on the Nanping triphylite has yielded the following results: Ng//b, Np//c, Nm//a. The test on the Keketuohai lithiophilite has yielded different results: Ng//b, Nm//c, Np//a. Both the Nanping triphylite and the Keketuohai lithiophilite belong to the rhombic system.

Fig. 3 represents the optical axial angle data of the five domestic samples and some other foreign samples (Samples No. 7, 12, 13, 16, 19, 20, 23 and 24 in Table 1). The curve in the diagram is taken from C. A. Chapman (1943)^[4]. As is indicated by the curve, the correlation between the 2V value and the Fe/Mn ratio in the minerals is generally satisfactory. There are three exceptions (Samples No. 1, 7 and 16 in Table 1). All the three have a relatively high Mg content and demonstrate a photonegative effect. This definitely means that the high Mg content greatly affects the optical properties of the minerals.

The correlation between the refraction index and the chemical composition is not very satisfactory. As is shown in Table 1, the general trend is that the three refraction indices rise when the Fe content increases.



[Key:] (1) Domestic samples
(2) Data on foreign samples (see Table 1)

4. Other Properties: In a microscopic view, the Nanping triphylite is colorless and transparent, with a glassy gloss, relatively even facets, a molar hardness value of 4--4.5, cleavage {100} complete, and {101} relatively complete. Under orthogonal polarization, it displays a Level 1 grayish white interference color, which does not demonstrate visible dispersion and is biaxial crystal photonegative. The Qinghe lithiophilite has similar properties. It is biaxial crystal photopositive, with a very small optical axial angle. Under orthogonal polarization, it often displays an abnormal interference color, which is bright ink blue or brownish red. The dispersion at the optical axial angle is detectable, $r > v$. Other minerals in this series have similar properties like the two samples discussed here. In addition, the authors have noticed that the "b" axis of the minerals in this series goes in the same direction as Ng without any exception. However, the "a" axis in lithiophilite goes in the direction of Np, but, in the case of triphylite, it goes in the direction of Nm (Fig. 3). This feature offers a quick indication whether the mineral is triphylite or lithiophilite.

IV. X-Ray Diffraction Analysis

1. X-Ray Powder Diffraction: An X-ray powder diffractometer was used to conduct X-ray powder diffraction analysis on the triphylite-lithiophilite samples from four domestic occurrences. The results are presented in Table 2. In the table, "A Place in Xinjiang" refers to a location whose identity information is lost. Due to the fact that the available quantity of samples was limited, only the X-ray analysis and the Mn simple-item analysis were performed: MnO=31.3%. The four samples have similar diffraction peaks in Table 2. From Sample No. 1 to Sample No. 6, the "d" value shows a visible rising trend.

2. Unit Cell Parameters: A computer was used to process the sample data discussed above. The computation yielded the unit cell parameters of each sample

(Table 3). The authors also collected data on four foreign samples for comparison. One of the foreign samples was a man-made pure $\text{LiFe}[\text{PO}_4]$ sample.

Fig. 4 shows the correlation between the cell parameters of the series minerals and their composition variations. The dotted line indicates the correlation between the cell parameters and the molecule count of the synthetic mineral $\text{LiMn}[\text{PO}_4] + \text{LiFe}[\text{PO}_4]$ without any influence from cations^[3]. As is indicated in the diagram, the "a", "b" and "c" values substantially decrease as the $\text{LiFe}[\text{PO}_4]$ molecule count of the minerals increases. It is obviously a linear correlation, as is indicated by the solid line in Fig. 4. The "a" value and the $\text{LiFe}[\text{PO}_4]$ molecule count have a very satisfactory negative correlation, yielding a correlation coefficient of -0.993. Most of the dots are below the dotted line in the diagram. This is probably because the minerals have a relatively high percentage of Mg^{3+} and Fe^{3+} . Mg^{2+} and Fe^{2+} have a shorter ionic radius than Mg^{3+} and Fe^{3+} . This characteristic probably lies behind the fact that the "b" value of the Nanping triphylite is very small. Of course, measuring errors may have to be taken into consideration, too.

表 2. 磷铁锂矿-磷锂矿系列X射线粉末衍射数据
Table 2 X-ray powder diffraction data of triphylite-lithiophilite series

① 序号 No.	② 峰位 Peak	③ 强度 Intensity	④ 峰位 Peak	⑤ 强度 Intensity	⑥ 峰位 Peak	⑦ 强度 Intensity	⑧ 峰位 Peak	⑨ 强度 Intensity
020	5.141	15	5.171	17	5.174	15	5.180	18
011	4.359	44	4.283	48	4.289	35	4.299	31
	3.951	20	3.828	17	3.840	11	3.833	10
101	3.729	13	3.711	9	3.710	8	3.719	8
111	3.470	54	3.503	52	3.498	49	3.501	55
200	3.892	98	3.021	94	3.025	100	3.035	100
031	2.768	57	2.785	83	2.791	27	2.784	31
	2.546	26						
131	2.514	100	2.531	100	2.534	72	2.538	81
211	2.462	38	2.468	34	2.475	25	2.480	29
	2.387	13	2.382	20	2.387	15	2.398	17
	2.363	19					2.387	15
	2.285	17	2.207	17	2.200	12	2.203	16
230	2.257	30	2.271	29	2.275	20	2.278	23
112	2.135	21	2.146	20	2.150	18	2.155	17
141	2.068	9						
231	2.073	6	2.047	16	2.052	5	2.051	9
122	2.023	6	2.020	7	2.024	6	2.029	6
	1.895	5						
	1.884	8						
202	1.845	19	1.858	12	1.862	10	1.866	11
311	1.810	15	1.804	17	1.829	14	1.834	15
241	1.798	9						
222	1.738	39	1.751	32	1.754	25	1.755	33
142	1.652	24	1.677	21			1.684	16
	1.650	23	1.668	19			1.669	18
331	1.622	22	1.632	12	1.637	15		
	1.580	14	1.592	12	1.597	9	1.601	9
	1.488	38	1.500	10			1.509	21

⑦ 测试条件: $\text{CuK}\alpha$, 45kV, 50mA. ⑧ 测定者: 地矿部矿产研究所林月英。

- [Key:]
- (1) Sample No.
 - (2) Place of Origin
 - (3) Nanping, Fujian
 - (4) Qinghe, Xinjiang
 - (5) A Place in Xinjiang
 - (6) Keketuohai, Xinjiang
 - (7) Test conditions:
 - (8) Tests conducted by Lin Yueying, Mineral Deposit Research Institute, Ministry of Geology and Mining Industry.

表 3 磷铁锂矿-磷锂辉石系列的晶胞参数 (Å)

Table 3 Cell dimensions of triphylite-lithiophilite series

样 号	1	5	6	9	10	11	12	13
产 地	福建南平	新疆青河	新疆条地	新疆可可托海	芬兰	瑞典	加利福尼亚	合成矿物
资料来源	3	7	作	8	(10)	(12)	(18)	(23)
时 间	4	1987			1974	1967	1985	1987
$\frac{Fe \times 100}{Fe + Mn}$	88.6	50.1	90.6	100	70.7	65.9	17.8	100.0
a	6.005	6.049	6.072	6.082	6.025	6.038	6.074	5.997
b	10.120	10.880	10.614	10.290	10.35	10.374	10.451	10.314
c	4.700	4.720	4.781	4.716	4.706	4.711	4.721	4.686
V	285.6	296.4	299.1	284.6	292.4	286.1	299.7	268.8

测试者: 地矿部矿床所林月英。 14

- [Key:]
- (1) Sample No.
 - (2) Place of Origin
 - (3) Source of Information
 - (4) Year
 - (5) Nanping, Fujian
 - (6) Qinghe, Xinjiang
 - (7) Authors of This Article
 - (8) A Place in Xinjiang
 - (9) Keketuohai, Xinjiang
 - (10) Finland
 - (11) Sweden
 - (12) California
 - (13) Synthetic Mineral
 - (14) Tests conducted by Lin Yueying, Mineral Deposit Research Institute, Ministry of Geology and Mining Industry.

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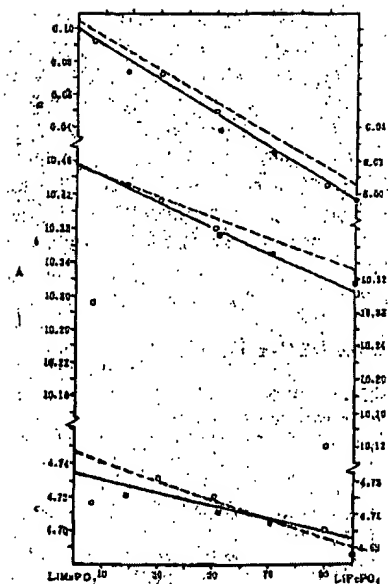


图 4 磷铁锂矿-磷锂矿的晶胞
参数与成分间关系

Fig. 4 Unit cell dimensions versus chemical
composition of triphylite-lithiophilite series

① 为国内样品 ② 为国外资料 (见表3)

①

②

[Key:] (1) Domestic samples
(2) Data on foreign samples (see Table 1)

V. IR Absorption Spectral Analysis

IR absorption spectra of triphylite were published by Moenke^[24], Sadtler Lab^[25], and Peng Wenshi and Liu Gaokui^[26]. Zhang Rubo published an IR spectrum of the lithiophilite in the Xiaohusite pegmatite in Xinjiang^[8]. Farmer assigned the vibration spectra for $M^I M^{II} [PO_4]$ compounds (triphylite-lithiophilite minerals are in this category)^[27]. The three high-strength absorption spectral bands in the range of $1141\text{--}1044\text{cm}^{-1}$ are for the asymmetric stretching vibration of $[PO_4]^{3-}$. The one spectral band in the range of $990\text{--}979\text{cm}^{-1}$ is for the ν_1 symmetric stretching vibration of $[PO_4]^{3-}$. The three medium-strength absorption spectral bands in the range of $641\text{--}549\text{cm}^{-1}$ are for the ν_4 bending vibration of $[PO_4]^{3-}$. The two absorption spectral bands in the range of $470\text{--}405\text{cm}^{-1}$ are for the ν_4 bending vibration of $[PO_4]^{3-}$. No published reports have been available on the IR spectral study of the isomorphous replacement in triphylite-lithiophilite minerals.

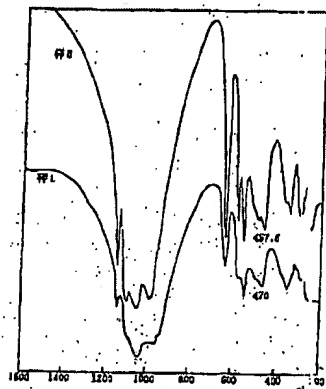


图 5 磷铁锂矿-磷锂矿系列矿物的红外吸收光谱图
Fig. 5 IR spectra of triphylite-lithiophilite series
((1), 磷铁锂矿; (2), 磷锂矿)

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[Key:] (1) (Samples No. 3 and 6 have similar properties, which will not be dwelt upon herein.)

The authors have conducted IR absorption spectral analysis study of four triphylite-lithiophilite mineral samples from different places of origin and with different Fe(Mn) contents (Fig. 5). Table 4 lists the main absorption spectral band frequencies. The analysis has revealed that the absorption spectral band frequencies decrease as the $\text{LiFe}[\text{PO}_4]$ molecule count decreases in the minerals. The eighth spectral band has shown the most systematic changes. Fig. 6 shows the correlation between the eighth spectral band and the $\text{Fe}/(\text{Fe}+\text{Mn})$ ratio in the minerals. As is indicated in Fig. 6, the ν_4 bending vibration spectral band in the range of $475\text{--}455\text{cm}^{-1}$ and the Fe and Mn replacement in the minerals has a very satisfactory linear correlation, which may be expressed in the following equation:

$$\nu(\text{cm}^{-1}) = 0.1473 \left(\frac{100 \times \text{Fe}}{\text{Fe} + \text{Mn}} \right) + 456.8$$

The correlation may have a coefficient of 0.9992. However, due to the limited quantity of samples, information in this respect needs to be supplemented.

表 4 磷铁锂矿-磷锰锂矿红外吸收光谱频率 (cm^{-1})

Table 4 Absorb peaks along IR spectra of triphylite-lithiophilite series

样号	产地	$\frac{\text{Fe} \times 100}{\text{Fe} + \text{Mn}}$	1	2	3	4	5	6	7	8
1	福寿南平	88.9	1141	1064	1051	990	841	580	552	470
2	新疆奇台	50.1	1137	1085	1048	984	838.5	578	549	464
3	新疆柯舍木特	19.1	1138	1092	1044	987	839	577	550	458
4	新疆可可托海	6.1	1134.5	1091.5	1047	978	837.5	576	549.5	457.5

测试条件: 岛津IR-450红外分光光度计, KBr混合压片。
测定者: 地矿部地质研究所郭文合。

[Key:] (1) Sample No.
(2) Place of Origin
(3) Nanping, Fujian
Qinghe, Xinjiang
Kelumute, Xinjiang
Keketuohai, Xinjiang
(4) Test conditions: Shimazu IR-450 IR spectrophotometer; K.Br hybrid press plates.

Tests conducted by Guo Wenhe, Mineral Deposit Research Institute, Ministry of Geology and Mining Industry.

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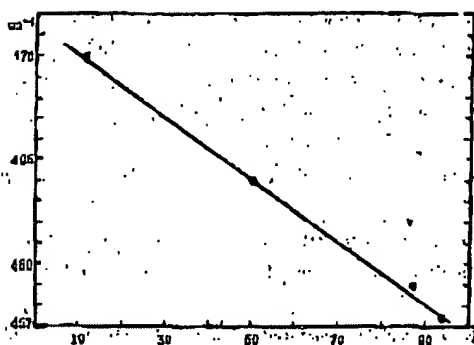


图 6 磷铁锂矿-磷锰锂矿中
频率在475—455cm⁻¹的红外吸收谱带
与成分间关系

Fig. 6 Correlation between
composition and IR absorb peaks
from 475 to 455cm⁻¹ in triphy-
lithiophilite series

VI. Conclusion

1. The triphylite found in the Nanping rare-metal granite pegmatite is one of the few triphylite deposits closest to the Fe end member in nature. A lithiophilite deposit with the Fe/Mn ratio nearly at 1 has also been found in the Qinghe pegmatite in Xinjiang. Those two occurrences, together with four other triphylite-lithiophilite discoveries, constitute a relatively complete isomorphous series of those minerals in China.

2. Studies on the chemical compositions of those minerals have revealed that Mg²⁺ and Ca²⁺ may, in a partial isomorphous reaction process, replace Fe²⁺ and Mn²⁺ in those minerals. Generally speaking, Mg²⁺ is more likely to replace Fe²⁺ while Ca²⁺ is more likely to replace Mn²⁺. So far no discovery has been announced of native pure LiFe[PO₄] with the Fe content at its octahedral M(2) site being no more than 80%. On the other hand, high-purity LiMn[PO₄] does exist in nature. In triphylite minerals, Fe²⁺ is easily transformed to Fe³⁺ through oxidation and then enters the crystal lattice by means of Li⁺ leaching and H₂O.

3. China's triphylite-lithiophilite series minerals have characteristics quite similar to those of their counterparts in foreign countries. Changes in the chemical compositions (especially the Fe/Mn ratio) will bring about systematic changes in the physical and optical properties and the unit cell parameters of the minerals. On the other hand, those property values may be used to determine, semi-quantitatively, the chemical compositions of the minerals. The method of measuring optical axial angles and determining optical directions usually yields satisfactory results.

4. Studies on the correlation between the chemical compositions of this series and their IR absorption spectra have revealed a satisfactory linear correlation between the absorption spectral band in the frequency range of 475-455cm⁻¹ and the mineral compositions: $\nu(\text{cm}^{-1}) = 0.1479(100 \times \text{Fe}/(\text{Fe}+\text{Mn})) + 456.8$. Therefore, it is of some practical significance to use IR spectra to indirectly determine the chemical compositions of this mineral series.

The authors wish to acknowledge the assistance and guidance from Yuan Zhongxin, Fellow at the Mineral Deposit Research Institute, Ministry of Geology and Mining Industry, and Yu Shiying, an engineer at the same institution.

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[Key to Items 5, 6, 20, 21, 22, and 26:]

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[Article No. 3]

[Only the beginning of the article is available in the original Chinese copy.]

Study on the IR Spectra of Wolframite Isomorphous Series*

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Key words: Wolframite, Isomorphous series, IR spectrum

* This article is a project sponsored by the Science Fund.

Abstract: *This article is part of a research project on the wolframite isomorphous series. Test results have revealed that the frequency and power of some absorption bands in the intermediate IR sector and the far IR sector have a satisfactory linear correlation with the relative content of two end members of the wolframite minerals (FeWO_4 and MnWO_4). The article presents the correlation equation and correlation chart about frequency variations. It also discusses the internal mechanism for frequency shifts and power variations.*

Wolframite is a complicated mineral which contains tungsten oxides. In the structure of wolframite, W^{6+} is connected not only to the four O^{2-} around it, but also to two other O^{2-} that are relatively far away, to form a $[\text{WO}_6]$ poly-octahedron^[1]. However, for the purpose of conducting comparative studies of the $[\text{WO}_6]$ poly-octahedron against the "free" morphological anions in the $[\text{WO}_4]^{2-}$ tetrahedron and the $[\text{WO}_4]^{2-}$ isolated tetrahedron in scheelite, and also out of the consideration that the two O^{2-} are too far away from the W^{6+} in the $[\text{WO}_6]$ poly-octahedron, it may be advisable to regard the $[\text{WO}_6]$ poly-octahedron as a $[\text{WO}_4]^{2-}$ tetrahedron. Like the $[\text{WO}_4]^{2-}$ isolated tetrahedron in scheelite and the "free" morphological anions in the $[\text{WO}_4]^{2-}$ tetrahedron, the wolframite $[\text{WO}_4]^{2-}$ also has four regular vibration modes^[2]: the symmetrical stretching vibration (ν_1), the out-of-plane bending vibration (ν_2), the anti-symmetric stretching vibration (ν_3), and the in-plane bending vibration (ν_4).

表 1 黑钨矿单矿物的化学成分

Table 1 Chemical composition of wolframite minerals

样品号	化 学 成 分 (重量%)							Fe/(Fe+Mn)	备注
	FeO	MnO	WO ₃	Nb ₂ O ₅	Ta ₂ O ₅	Sc ₂ O ₃	Σ		
P-7-49	8.55	17.52	74.81	0.159	0.014	0.013	98.17	0.241	4
P-8-49	8.83	17.02	74.62	0.203	0.041	0.009	98.03	0.269	
P-13-49	8.27	14.49	75.81	0.381	0.026	0.036	98.81	0.360	
P-13-49	4.67	17.85	74.55	0.058	0.000	0.007	97.16	0.205	
P-14-501	7.05	13.08	74.71	0.708	0.090	0.045	98.10	0.834	
P-15-501	9.41	13.36	75.35	0.250	0.018	0.022	98.41	0.410	
P-15-501	10.14	12.51	74.55	0.577	0.129	0.045	97.80	0.445	
P-17-501	5.58	10.89	74.01	0.380	0.076	0.028	96.89	0.244	
P-18-501	10.31	12.51	78.60	0.330	0.027	0.051	98.83	0.449	
P-3-35	9.18	14.12	75.17	0.274	0.097	0.025	98.87	0.391	5
P-4-35	6.70	16.75	76.28	0.169	0.030	0.009	99.91	0.288	
P-6-35	6.57	16.40	75.97	0.208	0.047	0.014	99.21	0.283	
P-7-35	7.44	15.81	75.19	0.257	0.102	0.023	98.83	0.316	
P-8-35	3.52	18.24	75.50	0.183	0.055	0.019	97.53	0.160	
P-11-35	7.08	16.16	75.08	0.125	0.018	0.014	98.48	0.302	
P-12-35	9.51	13.28	74.78	0.549	0.089	0.031	98.25	0.414	
V-140-10-1	2.45	20.18	75.41	0.204	0.007	0.003	98.85	0.107	
V-180-10-1	3.01	18.12	76.15	0.207	0.038	0.017	98.54	0.188	
V-180-10-2	3.19	18.13	75.50	0.152	0.039	0.003	98.48	0.198	6
V-190-10-3	2.20	18.11	74.83	0.250	0.011	0.005	97.18	0.098	
V-190-18-2	2.47	19.12	73.02	0.383	0.020	0.005	96.34	0.110	
V-338-10-3	1.98	20.17	75.28	0.130	0.018	0.005	97.87	0.086	
H-1	21.59	1.17	74.82	0.339	0.005	0.032	98.67	0.819	
SM-84*	13.87	10.17	78.13	0.108	0.031	未测	100.80	0.567	
W-3**	0.05	21.54	76.12	0.69	—	—	98.34	0.002	7
KS-23-10	11.83	11.00	75.85	0.80	0.13	—	99.50	0.515	
P-5-49	16.48	7.13	76.05	0.32	0.01	—	99.04	0.807	
KS-146-3	12.59	10.35	76.00	0.42	0.05	—	99.41	0.580	
D-3-1	12.63	9.01	76.88	1.08	—	—	100.40	0.575	
SP-77	15.85	7.02	75.80	0.02	—	—	98.80	0.692	
KS-146-3	16.34	5.81	75.45	0.39	—	—	98.01	0.714	
F-1	17.58	4.01	78.48	0.13	—	—	98.11	0.808	

* 由湖南省地矿局任和屈提供化学分析数据。

** W-2样品产于秘鲁。

化学分析：湖南省地矿局中心实验室化学分析室，电子探针分析：马鞍山矿山研究院包荣夫等。

- [Key:]
- (1) Sample No.
 - (2) Chemical Composition (wt%)
 - (3) Remarks
 - (4) Chemical Analysis
 - (5) Electronic Probe Analysis
 - (6) Not Tested
 - (7) * Chemical analysis data provided by Ren Xiangmei, the Geological and Mineral Bureau of Hunan Province.

** W-2 samples from Peru.

The chemical analysis was conducted by the Chemical Analysis Group in the Central Lab of the Geological and Mineral Bureau of Hunan Province.

The electronic probe analysis was conducted by Bao Rongfu and others at the Ma An Shan Mineral Deposit Research Institute.

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